

## Electronic supplementary information (ESI)

### Thermo-responsive amino acid-based vinyl polymers showing widely tunable LCST/UCST behavior in water†

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### **<sup>1</sup>H NMR analyses for NAA, NAF, and NAV**

**NAA** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 1.2-1.3 ppm (3H, -CHCH<sub>3</sub> : side chain of Ala), 4.2-4.3 ppm (1H, -COCHNH- : main chain of Ala), 5.6-5.7 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.3-6.4 ppm (1H, CH<sub>2</sub>CHCO- : vinyl), 8.4-8.5 ppm (1H, -CHNHCO- : amide), 12.4-12.8 ppm (1H, -COOH : calboxy).

**NAF** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 2.7-3.1 ppm (2H, -CHCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> : side chain of Phe), 4.3-4.4 ppm (1H, -COCHNH- : main chain of Phe), 5.5-5.6 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.2-6.3 ppm (1H, CH<sub>2</sub>CH- : vinyl), 6.8-7.3 ppm (5H, -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>- : side chain of Phe), 8.3-8.4 ppm (1H, -CHNHCO- : amide).

**NAV** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 0.8-1.0 ppm (6H, -CH(CH<sub>3</sub>)<sub>2</sub> : side chain of Val), 1.9-2.2 ppm (1H, -CHCH(CH<sub>3</sub>)<sub>2</sub> : side chain of Val), 4.0-4.3 ppm (1H, -COCHNH- : main chain of Val), 5.5-5.6 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.3-6.4 ppm (1H, CH<sub>2</sub>CHCO- : vinyl), 8.2-8.3 ppm (1H, -CHNHCO- : amide), 12.3-12.7 ppm (1H, -COOH : calboxy)

### **<sup>1</sup>H NMR analyses for NAAMe, NAFMe, and NAVMe**

**NAAMe** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 1.2-1.3 ppm (3H, -CHCH<sub>3</sub> : side chain), 3.6 ppm (3H, -COOCH<sub>3</sub> : methyl ester), 4.3-4.4 ppm (1H, -COCHNH- : main chain), 5.6 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.2-6.3 ppm (1H, CH<sub>2</sub>CHCO- : vinyl), 8.4-8.6 ppm (1H, -CHNHCO- : amide).

**NAFMe** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 2.9-3.1 ppm (2H, -CHCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> : side chain), 3.6-3.7 ppm (3H, -COOCH<sub>3</sub> : methyl ester), 4.5-4.6 ppm (1H, -COCHNH- : main chain), 5.6-5.7 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.2-6.3 ppm (1H, CH<sub>2</sub>CH- : vinyl), 7.2-7.4 ppm (5H, -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>- : side chain), 8.5-8.7 ppm (1H, -CHNHCO- : amide).

**NAVMe** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$  in ppm) : 0.8-0.9 ppm (6H, -CH(CH<sub>3</sub>)<sub>2</sub> : side chain), 2.0-2.1 ppm (1H, -CHCH(CH<sub>3</sub>)<sub>2</sub> : side chain), 3.6 ppm (3H, -COOCH<sub>3</sub> : methyl ester), 4.2-4.3 ppm (1H,

-COCHNH- : main chain), 5.6-5.7 ppm (1H, CH<sub>2</sub>CH- : vinyl (*cis*)), 6.0-6.1 ppm (1H, CH<sub>2</sub>CH- : vinyl (*trans*)), 6.3-6.4 ppm (1H, CH<sub>2</sub>CH- : vinyl), 8.3-8.4 ppm (1H, -CHNHCO- : amide).

Table S1 Results of copolymerization for the combination of NAG-NAA and NAGMe-NAAMe in DMF at 70°C for 12 h <sup>a</sup>

in feed(%)		in copolymer (%) <sup>b</sup>		in feed (%)		in copolymer (%) <sup>b</sup>	
NAG	NAA	NAG	NAA	NAGMe	NAAMe	NAGMe	NAAMe
50	50	45	55	100	0	100	0
25	75	35	65	75	25	83	17
10	90	15	85	50	50	56	44
5	95	9	91	25	75	33	67
0	100	0	100	0	100	0	100

<sup>a</sup> [total monomer] = 2.0 M; [AIBN] = 1.0 wt% to monomers. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

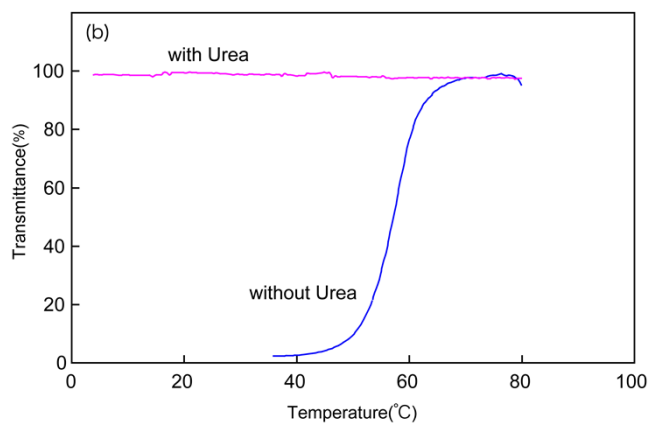
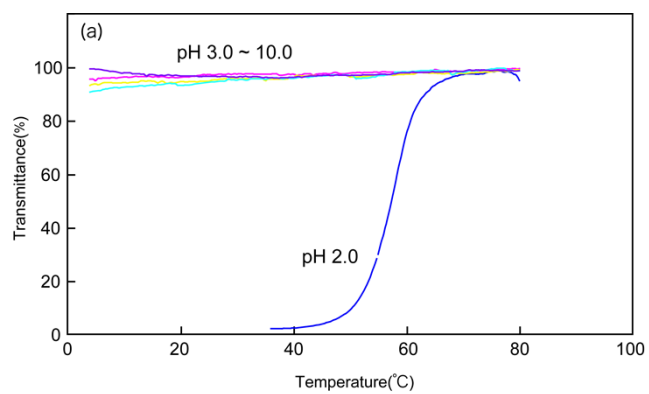


Fig. S1. Temperature dependence of the transmittance at 600 nm of aqueous solutions of PNAa at various pHs (a), and with and without urea (8 M) at pH 2.0 (b)